Fluorescence Emission Excitation Matrices (EEMs): Identifying Signatures for Constituents of Concern

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MWQI Face-to-Face Meeting
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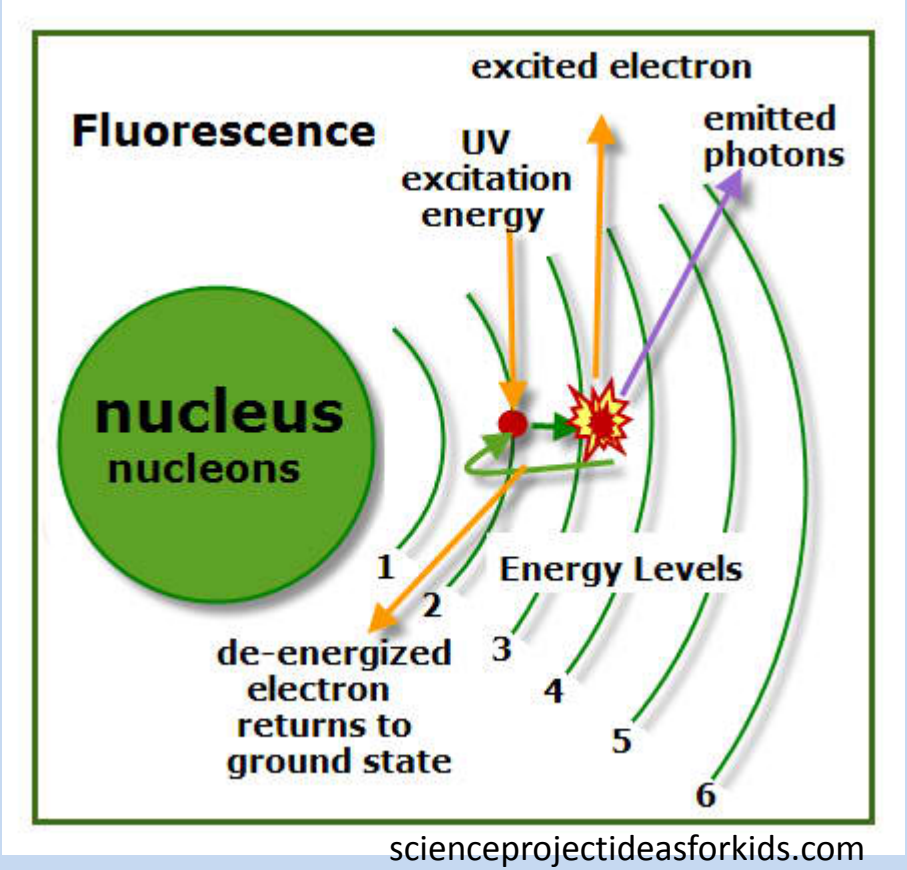
Outline

- What is spectrofluorescence and why use it?
  - Desire to find reliable, inexpensive methods to measure constituents
  - Brief Introduction to Spectrofluorescence
  - Application to measuring drinking water Constituents of Concern
- Spectrofluorometer Special Study
  - Goals, Study Design
  - Example Data
  - Progress & Next Steps

Spectrofluorescence Intro

- Fluorescence: When an electron is excited to a higher energy level (electron orbit) by absorption of light energy, and then releases energy as light as it drops to a lower energy level.



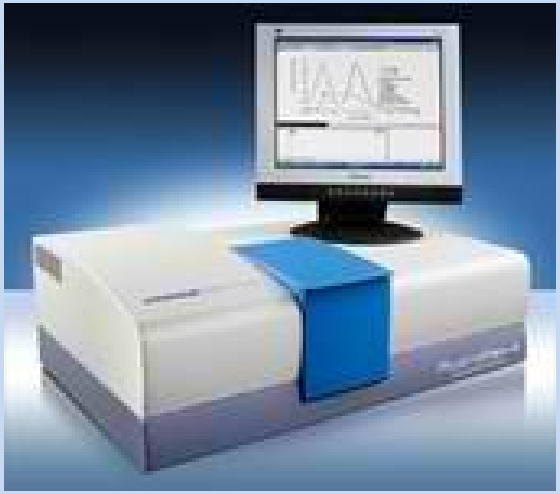
Intro, continued: Instruments

- A *fluorometer*: one pair of light wavelengths to measure, e.g., chlorophyll in algal cells.
  - Turner 10AU,
  - in-situ FDOM probe

Turner 10AU via act-us.info

Turner Cyclops-7 FDOM

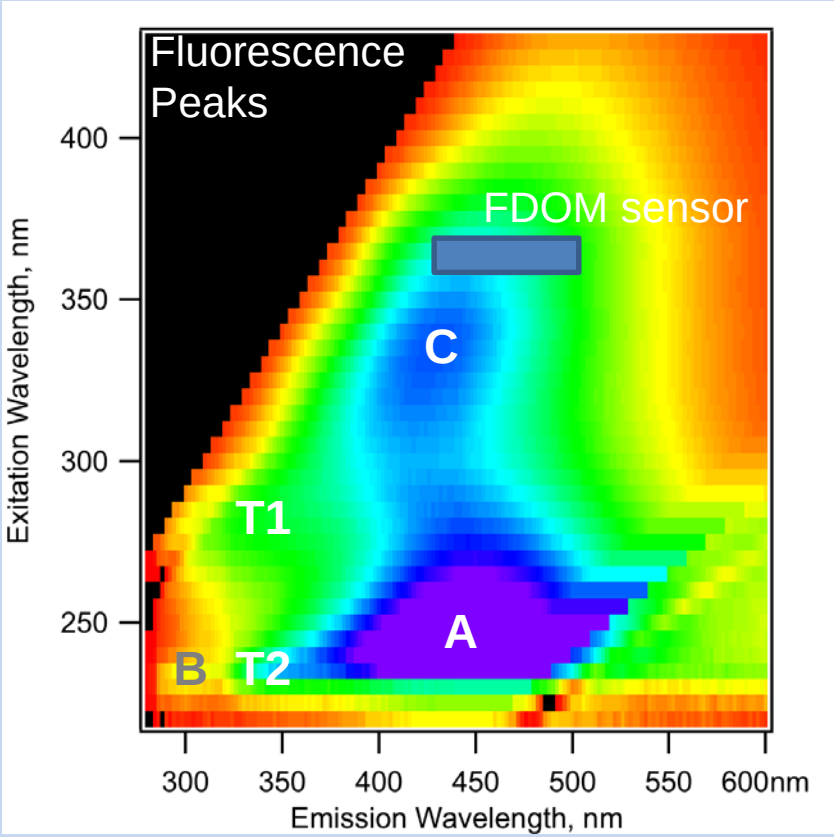
- A *spectrofluorometer*: Performs multiple measurements across bands of light wavelengths.
  - Horiba/Jobin-Yvon Fluoromax-4 purchased by QAQC Program.



Horiba Jobin-Yvon

Data: Excitation-Emission Matrix

Each *excitation-emission matrix (EEM)* consists of hundreds of measurement combinations of a single water sample, with excitation wavelength is on one axis, emission wavelength is the second, and fluorescence intensity forms a third axis.



Spectrofluorescence Special Study

- To investigate the usefulness of spectrofluor-escence as a way of quickly and easily quantify constituents of concern (CoCs) in source waters.
  - Organic carbon: Demonstrated
  - Nitrosamines: Possible?
    - Hua *et al*., 2007, *Fluorescence fingerprints to monitor total trihalomethanes and N-nitrosodimethylamine formation potentials in water. Environ Chem. Lett. 5:73–77*.
- Source water “fingerprinting”
  - Find distinctive fluorescence features in sources

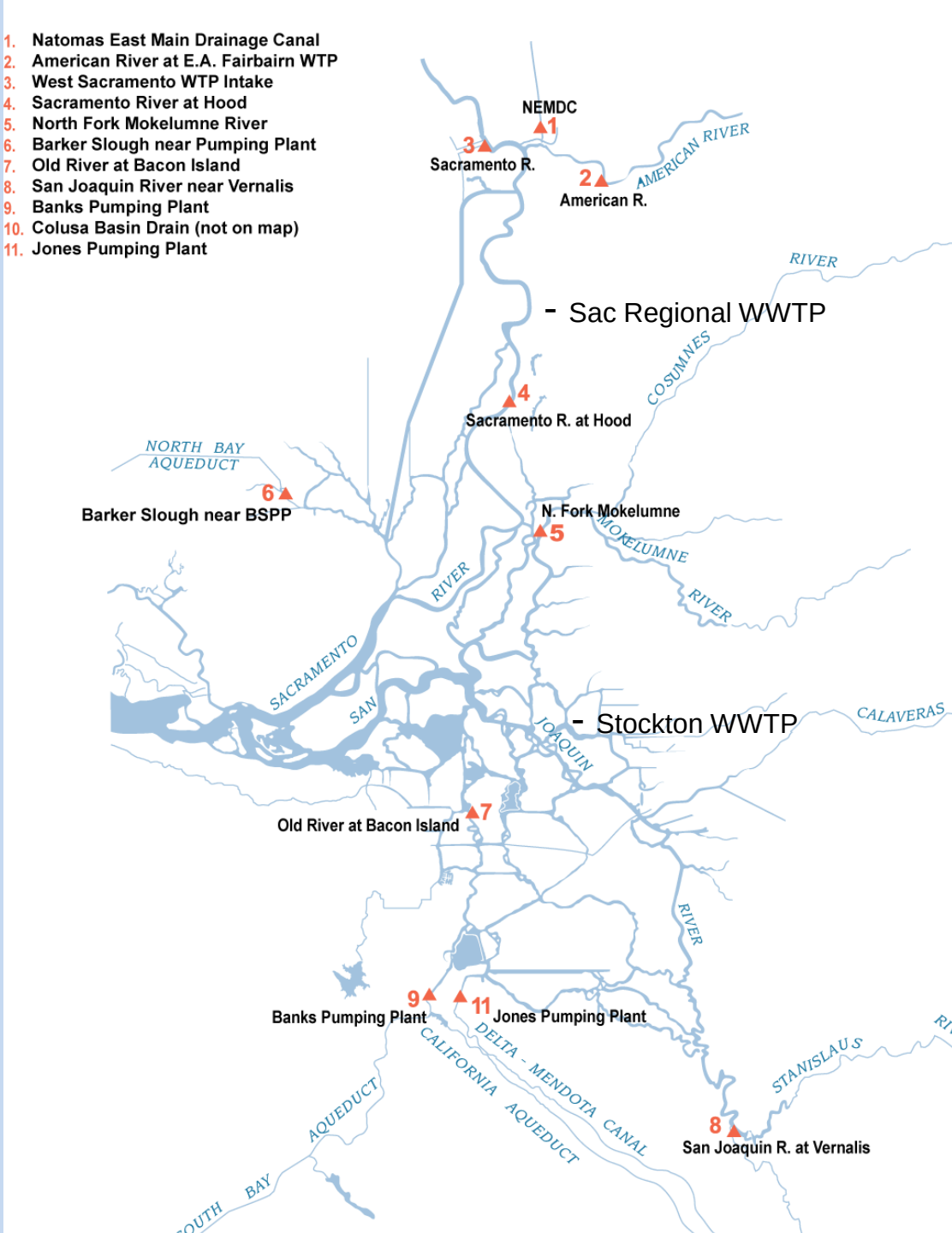
Study Design

- Two-year study, approved in the Work Plan
  - 11 stations sampled monthly (piggy-backed on MWQI routine sampling program), plus several other sites sampled at other frequencies.
  - Sample analysis for DOC, THMFP, HAAFP, Nitrogen chemical species, Spectrofluorescence EEM, Nitrosamine formation (~quarterly sampling).
  - Numerical analysis to identify features in the EEMs that correlate highly with Constituents of Concern.

Monthly Sampling Stations

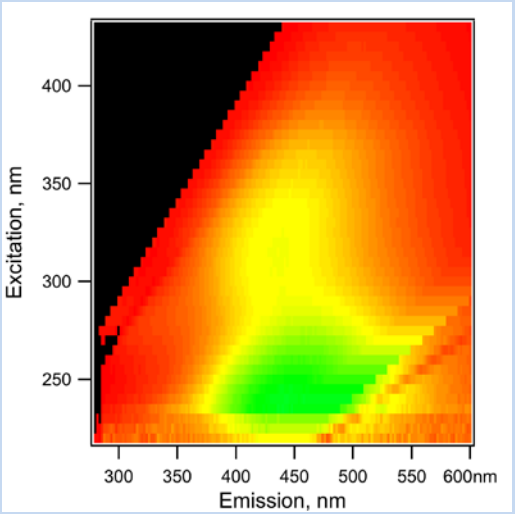
Represents:

- Major tributaries
- Seasonal variation
- Spatial variation
- Diff. Source waters
  - AMR “Pristine”
  - Colusa Ag runoff
  - NEMDC Urban
  - Waste Water

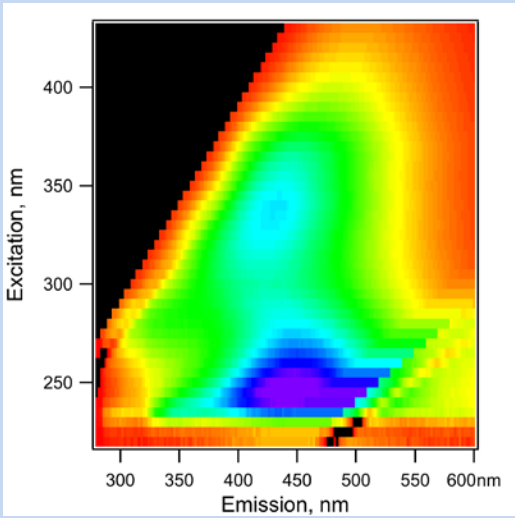


Example EEM Data: Spatial Variation

San Joaquin R, Downstream of Stockton WWTP 12 Sept 2011

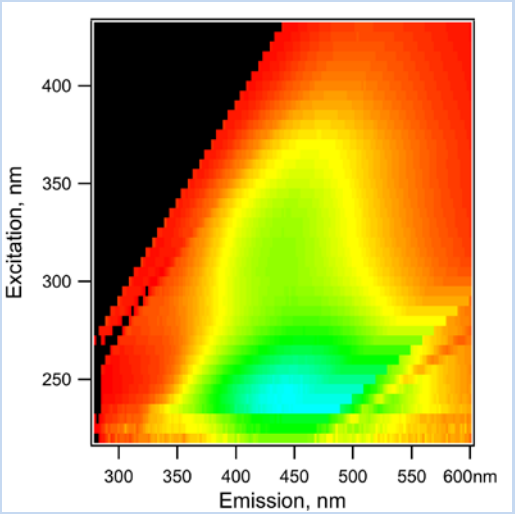


Stockton WWTP 05 Oct 2011



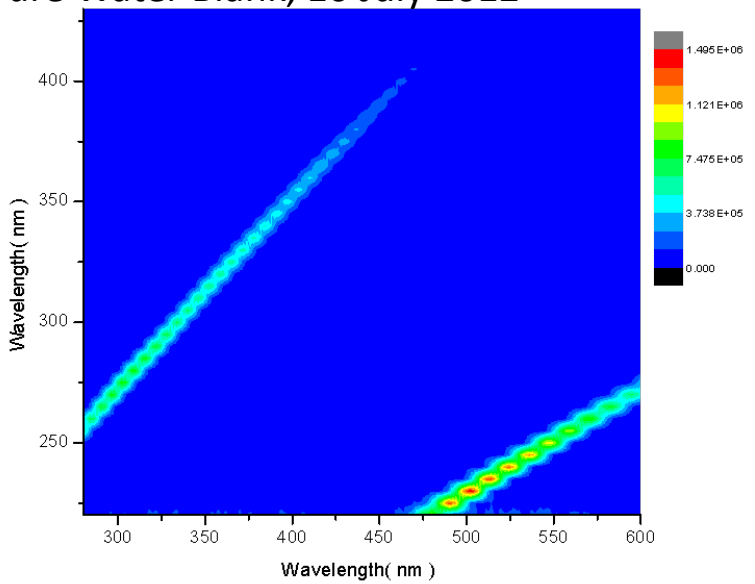
Natomas East Main Drain (NEMDC)

07 Mar 2011

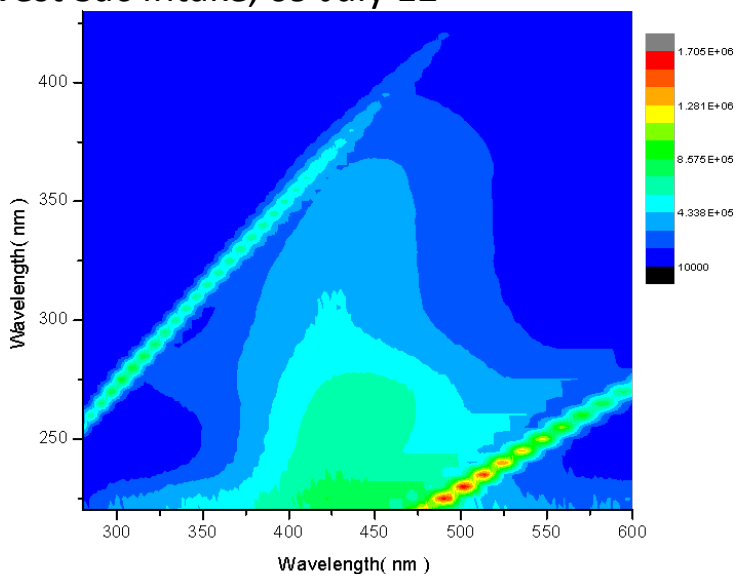


Example EEM Data: Spatial Variation

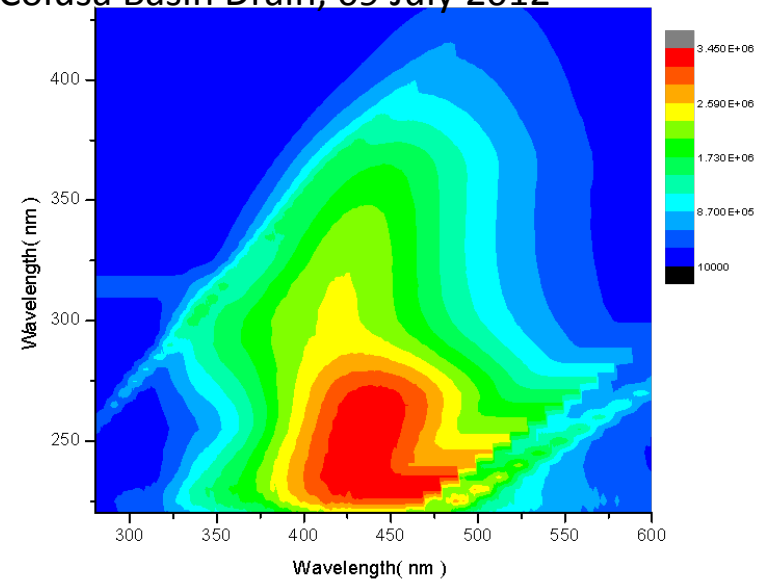
Pure Water Blank, 16 July 2012



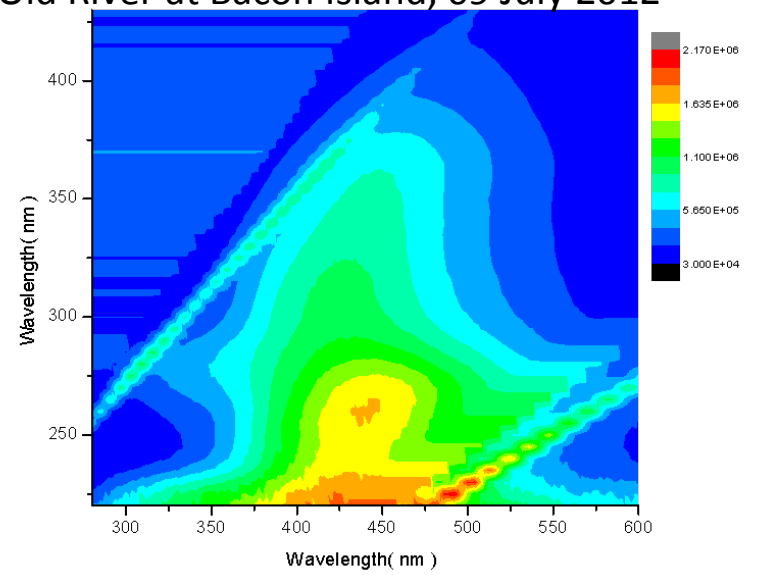
West Sac Intake, 09 July 12



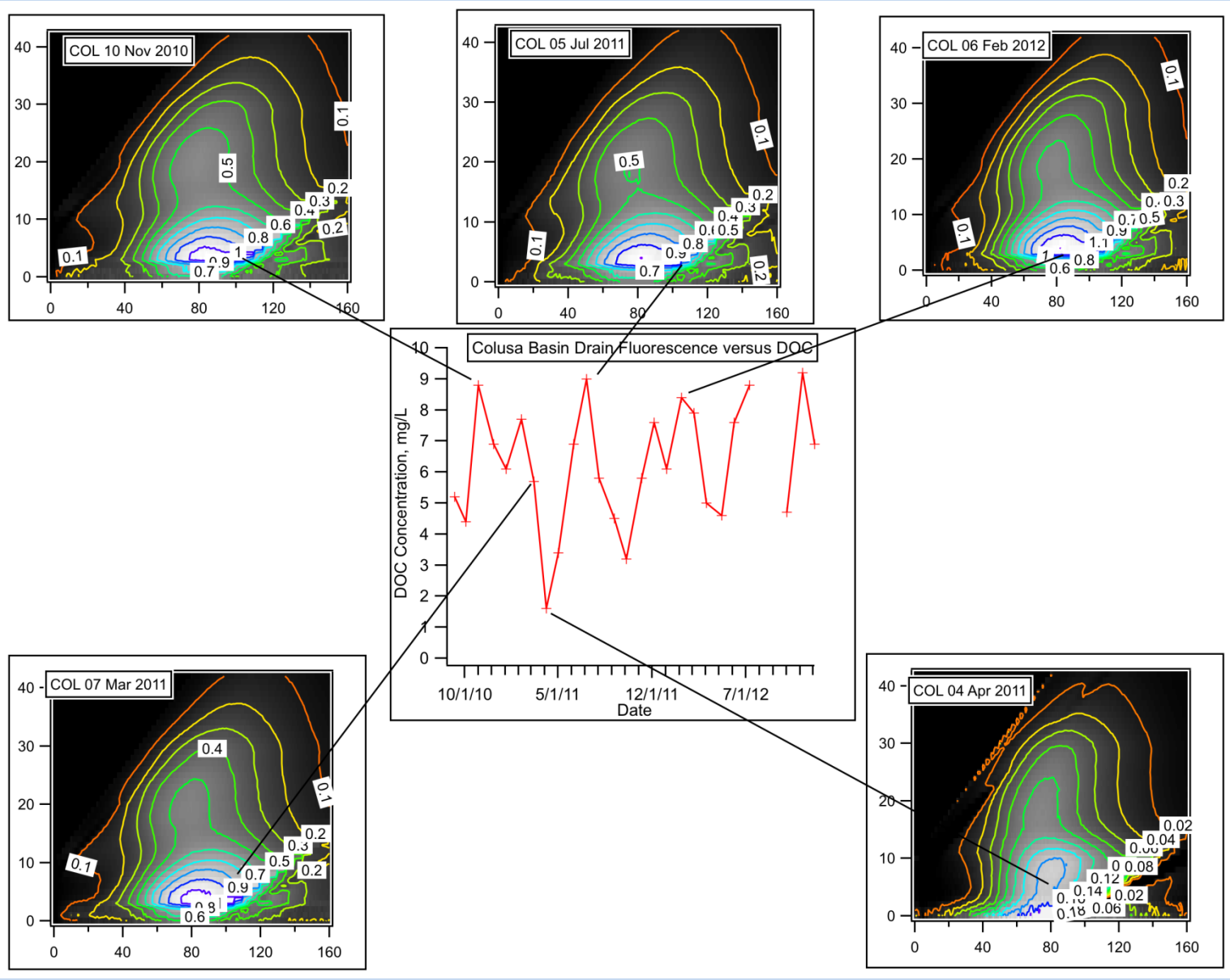
Colusa Basin Drain, 09 July 2012



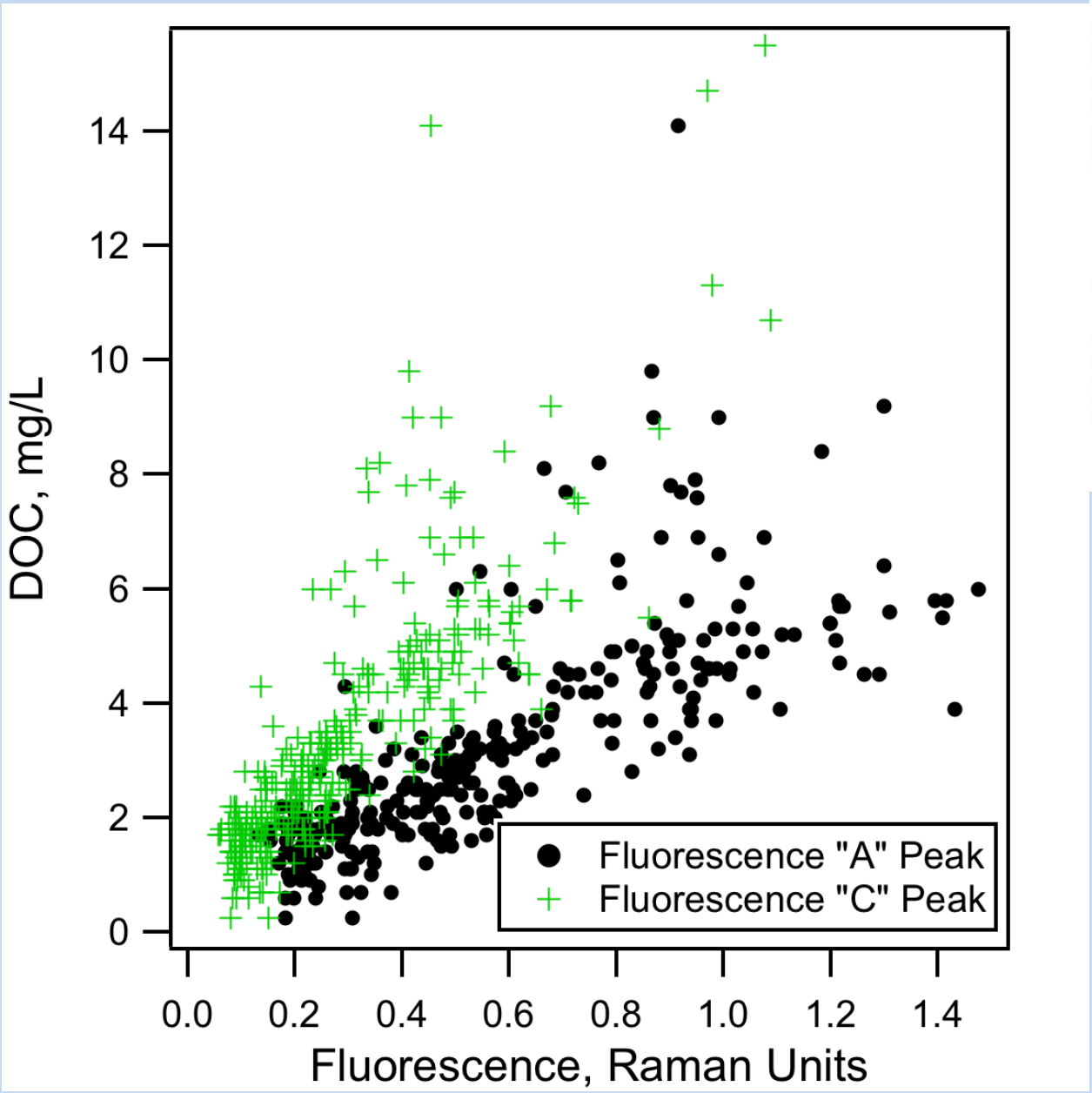
Old River at Bacon Island, 09 July 2012

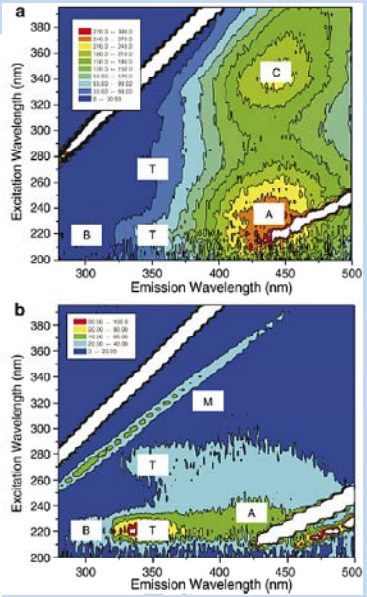


Example EEM Data: Time variation

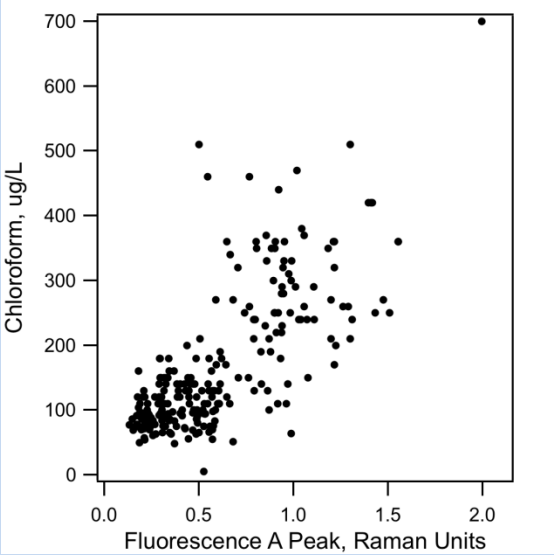


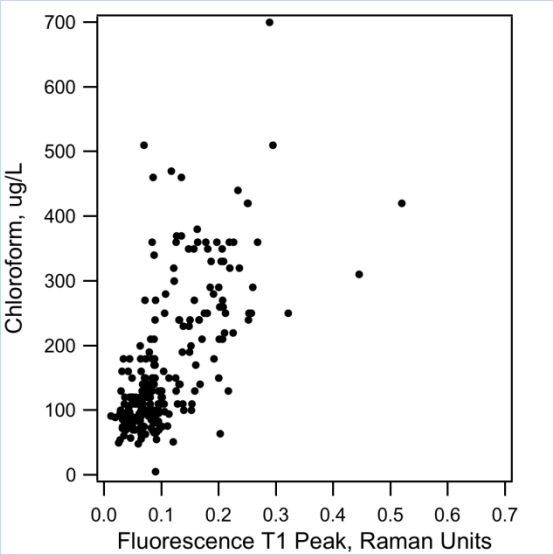
Example EEM Data: Correlation

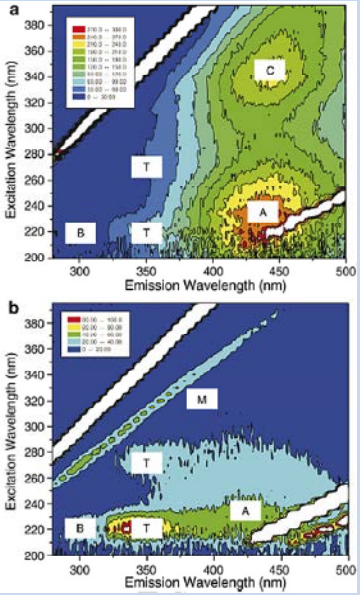


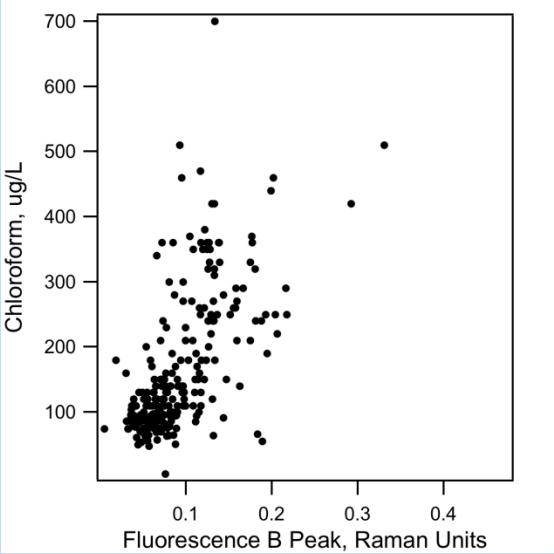


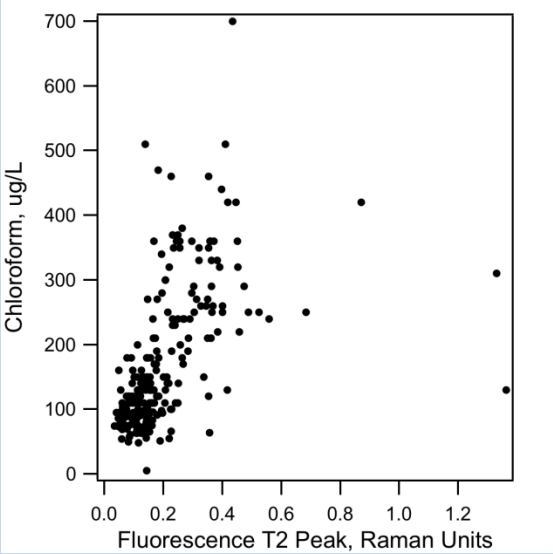
Chloroform and EEM features





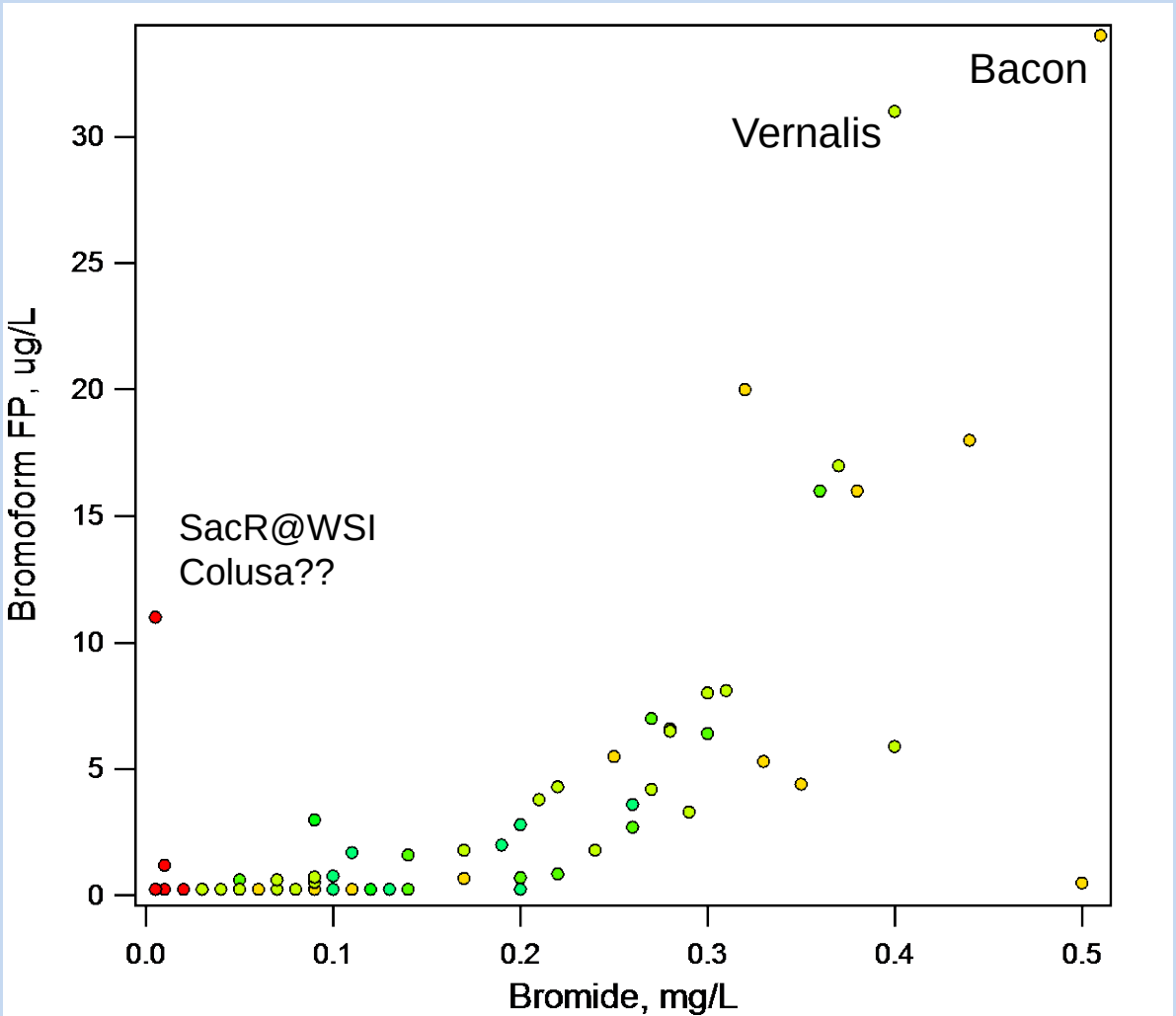


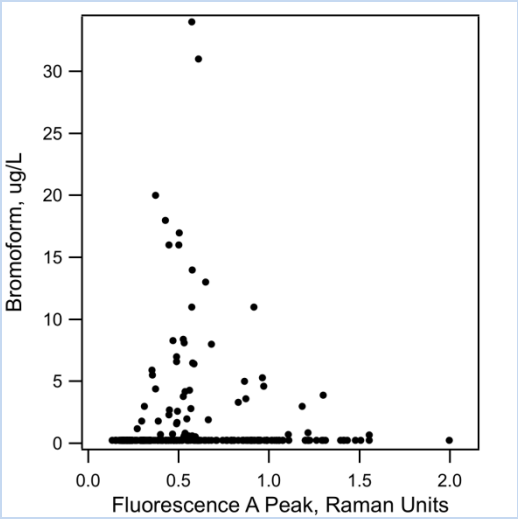




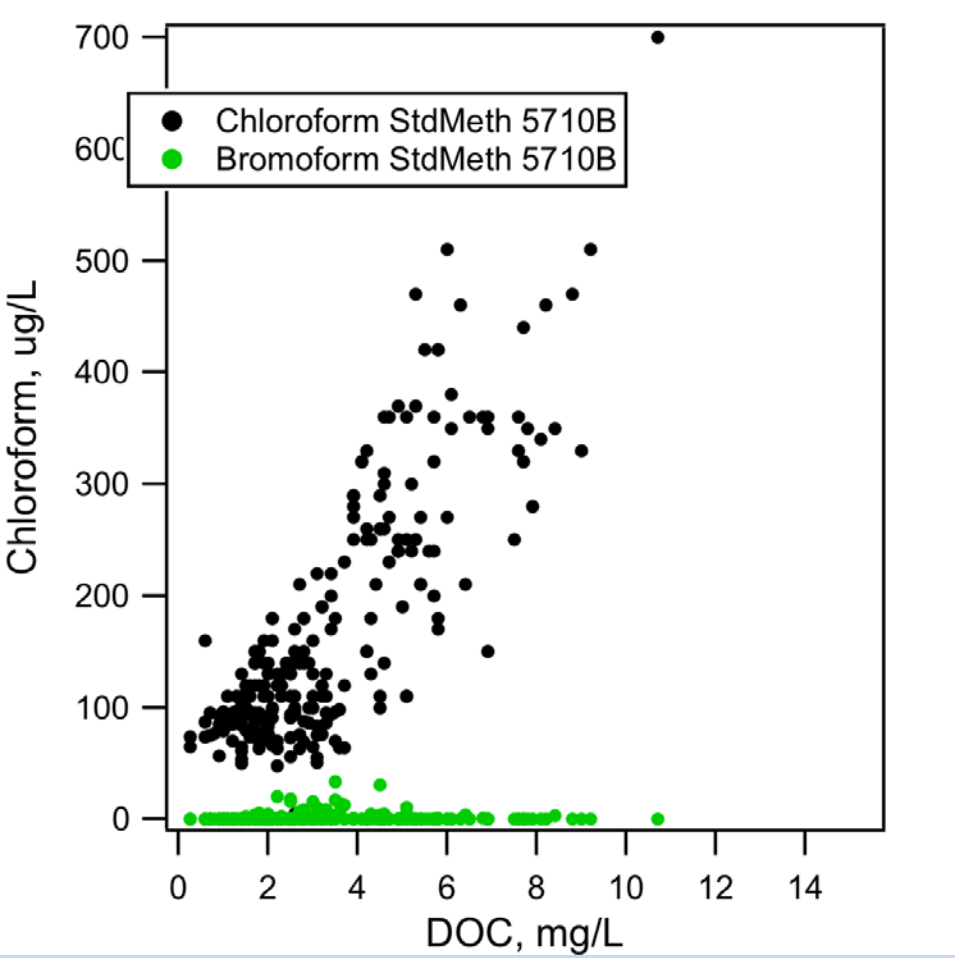
Bromoform and EEM features

- Mostly a function of source waters
- EEMs not very predictive of Bromoform FP

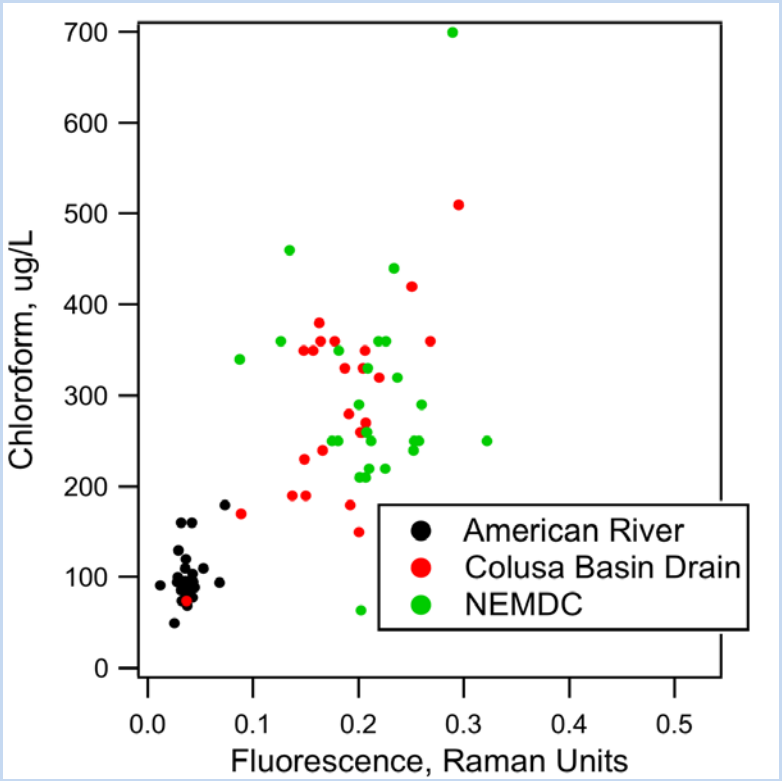


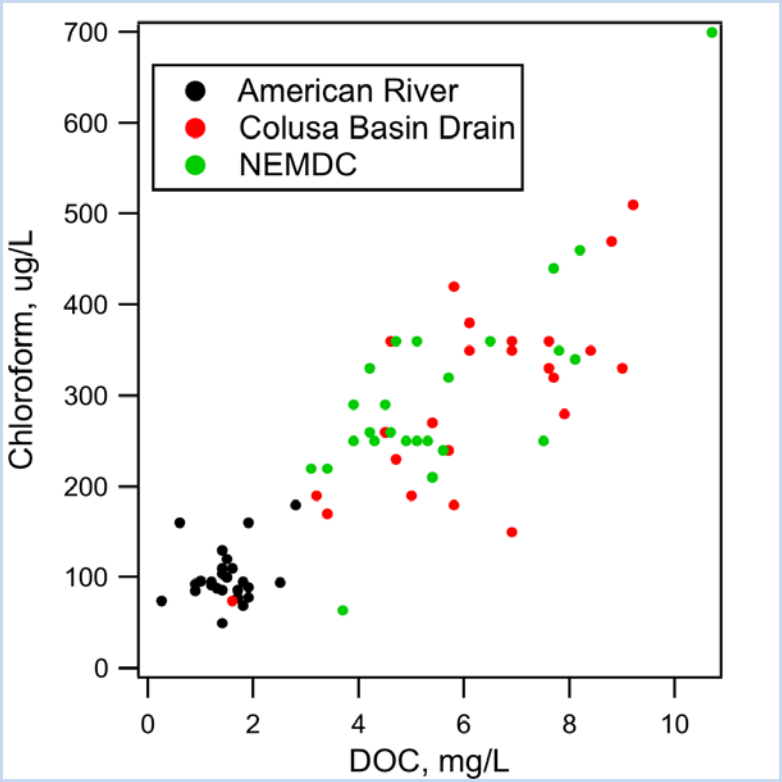


Halogens vs DOC

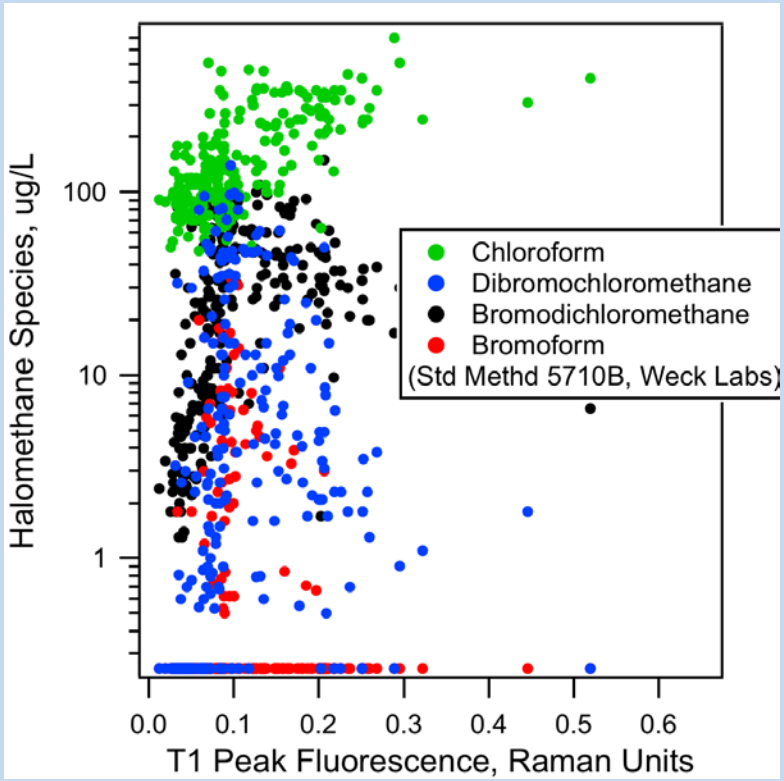


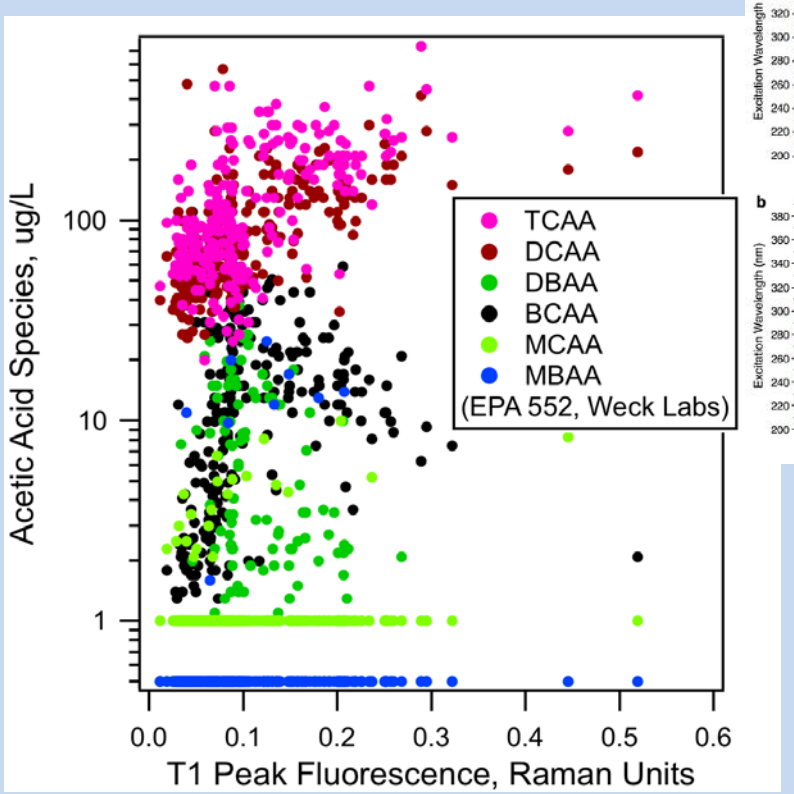
Chloroform variation

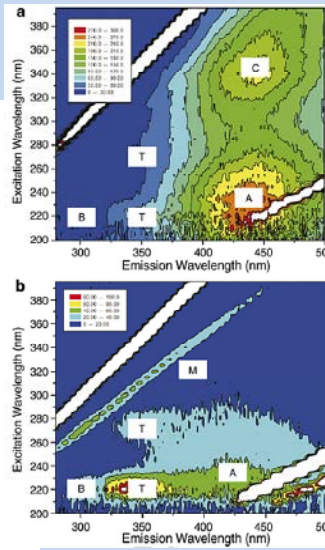




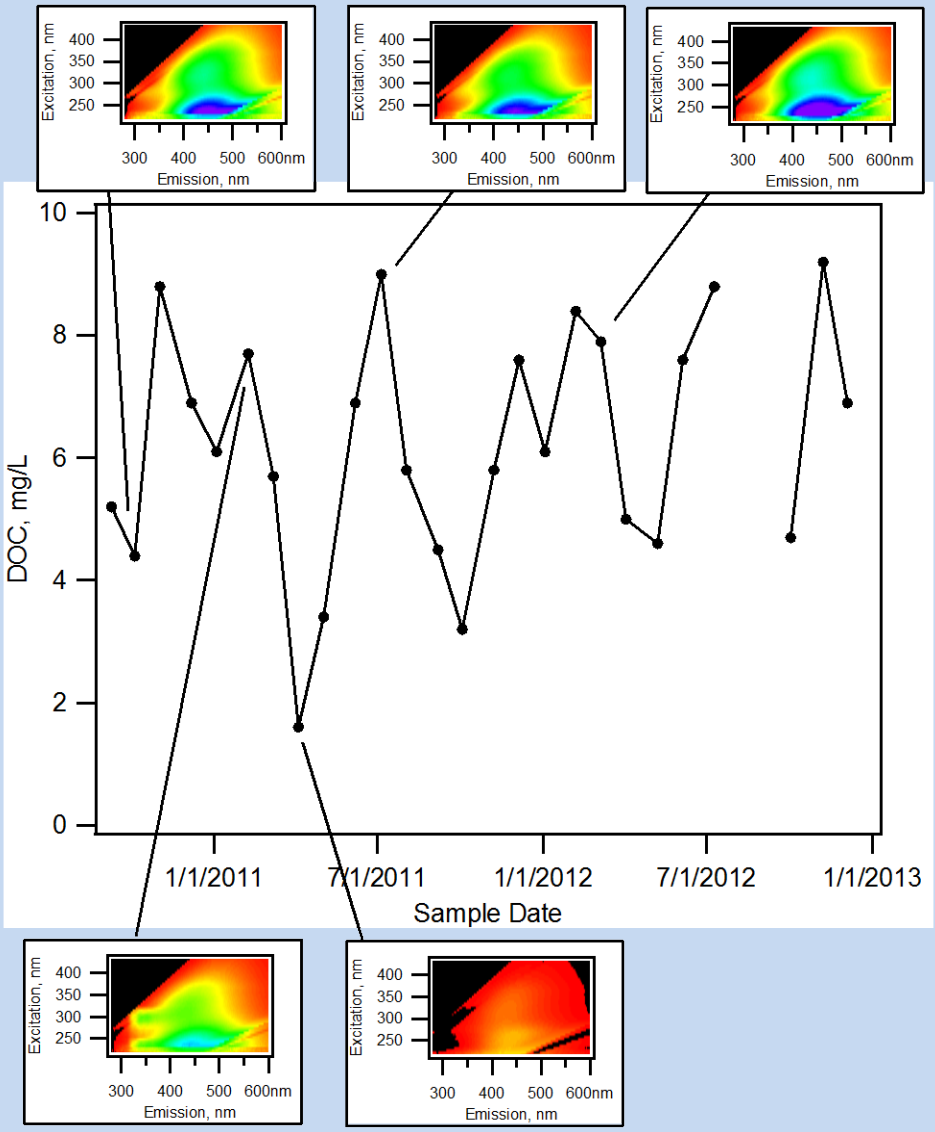
THMs & HAAs vs T1 Fluorescence



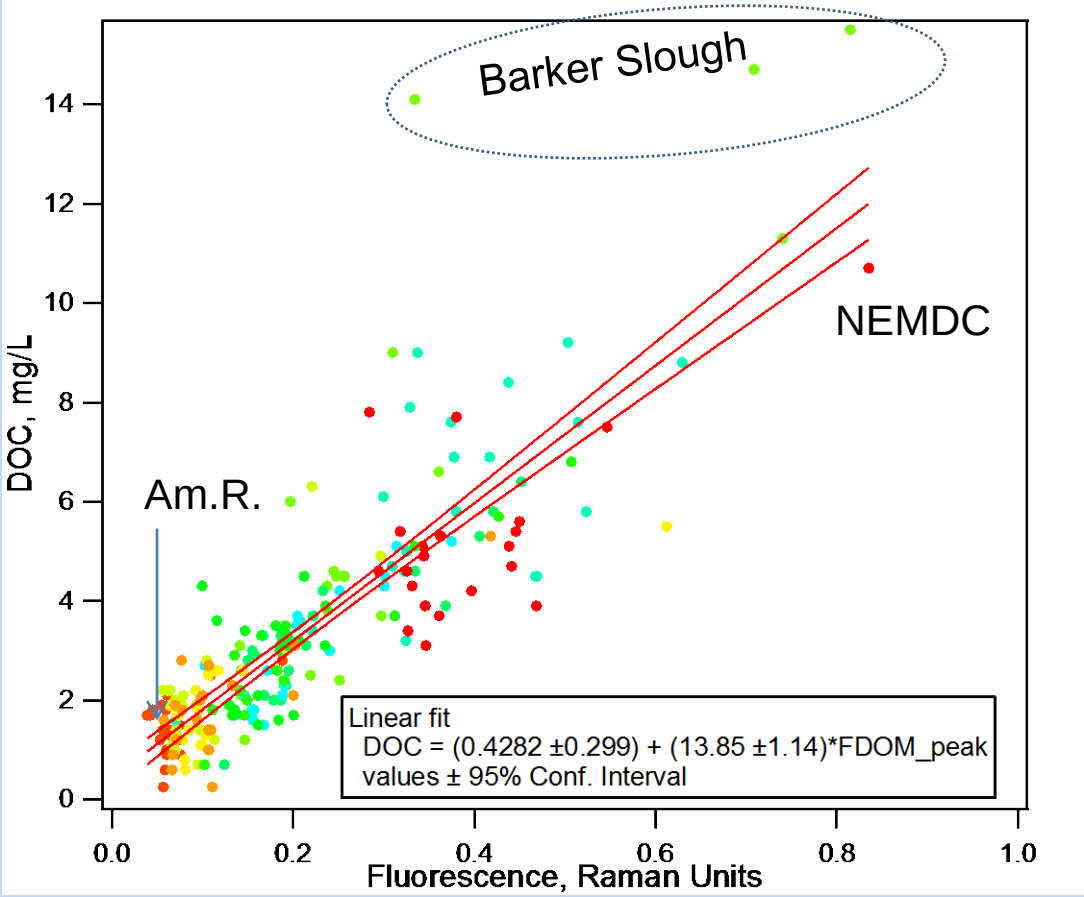


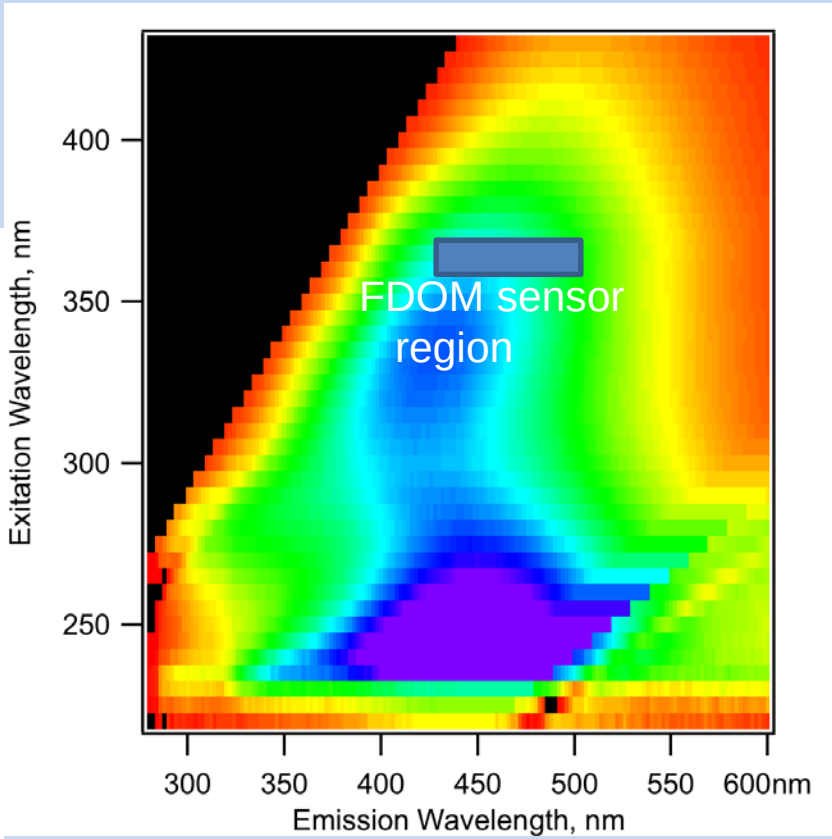


DOC


Excitation, nm
400
350
300
250
300 400 500 600nm
Emission, nm
DOC, mg/L
10
8
6
4
2
0
1/1/2011
7/1/2011
1/1/2012
7/1/2012
1/1/2013
Sample Date

Likely FDOM sensor response





Progress

- Successfully analyzing monthly water samples from 11 monthly + 8 other sites for Spectrofluorescence EEM, DOC, THMFP, HAAFP, Nitrogen chemical species likely to be nitrosamine precursors.
  - Nitrosamine correlation pending.
- Products: Final study report, feasibility for future monitoring, peer-reviewed article

- Acknowledgements:
  - MWQI Field Support Unit: Steve, Arin, Mark, Ken, Eric
  - Otome Lindsey: Fluorescence analysis
  - Murage Ngatia: Fluoromax 4 purchase, Collaboration, QAQC advice
  - Joe Christen: Additional sampling & Collaboration
  - Prof. James Sickman, UC Riverside: experiment design
  - Craig Nelson, UC Santa Barbara: software adaptation
  - Stuart Krasner, MWD: Nitrosamine collaboration
  - Bryte Laboratory, Weck Laboratory: CoC lab analysis

Questions & Comments?

References

Selected References

Hua, Bin, Kristen Veum, Amod Koirala, John Jones, Thomas Clevenger and Baolin Deng. 2007. Fluorescence fingerprints to monitor total trihalomethanes and N-nitrosodimethylamine formation potentials in water. Environ Chem. Lett. 5:73–77.

Hudson, Naomi A., Andy Baker, and Darren Reynolds. 2007. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters —A Review. River Research And Applications 23: 631–649.

Spencer, Robert G.M., Andy Baker, Jason M.E. Ahad, Gregory L. Cowie, Raja Ganeshram, Robert C. Upstill-Goddard and Günther Uher. 2007. Discriminatory classification of natural and anthropogenic waters in two U.K. estuaries. Science of the Total Environment 373:305–323.